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ECOLOGY AND ANALYSIS
OF TRACE CONTAMINANTS

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4. ECOLOGICAL RESEARCH

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4.1 Introduction

The Ecological Research Section of the EATC Program is composed of
three major research areas: Holston River–Cherokee Reservoir Studies,
Walker Branch Watershed Studies, and Crooked Creek Watershed Studies.
The scientific leaders for each of these areas are, respectively, S. G.
Hildebrand, S. E. Lindberg, and D. R. Jackson. Research activities in the
Holston River–Cherokee Reservoir System have been focused on determining
the biogeochemical cycling and transport of mercury released from the
waste disposal areas of a defunct chloro-alkali plant in Saltville,
Virginia. Walker Branch Watershed Studies have been designed to iden-
tify and evaluate the atmospheric input and hydrologic output of coal-
fired power plant derived trace elements deposited on the forested
landscape. Crooked Creek Watershed Studies have been concerned with
physical and biological transport of Cd, Pb, Cu, and Zn emitted from a
lead smelter in southeastern Missouri. Our work in Crooked Creek has
also lead to the identification of several ecosystem level effects of
these trace elements.

Successful attainment of our research objectives in these three
study sites has depended strongly upon the development of analytical
measurement techniques for determinations of elemental concentrations
and chemical speciation in a variety of environmental samples (see

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[a]Task Leader.

Section 5). Application of the Unified Transport Model (Section 3.3) to both Walker Branch and Crooked Creek Watersheds has depended upon accurate determination of parameters describing the movement of trace elements through these landscapes. One of our objectives in the Ecological Research area has been to provide these parameter estimates - as well as to participate in the development and modification of transport models depicting elemental flows through soils, soil water, and vegetation.

The primary objectives of the Ecological Research area include 1) development of techniques for evaluating trace element transport through ecosystems, 2) application of these techniques to areas contaminated by industrial emissions, and 3) incorporation of this information into the development of mechanistic ecological models for incorporation into the Unified Transport Model. In the following sections, we present our technical accomplishments for the period since our previous report.[1]

4.2 Holston River - Cherokee Reservoir Studies

4.2.1 Introduction and Methods. The North Fork of the Holston River (NFHR) originates in southwest Virginia, flows southwest into Tennessee, and after confluence with the South Fork, forms the main Holston River. The Holston River was impounded in 1942 forming Cherokee Reservoir (Fig. 4.1). A chlor-alkali plant located on the North Fork Holston River at Saltville, Virginia (approximately 277 km upstream from Cherokee Dam) in the 1950's began using a mercury cathode in the electrolytic separation of sodium chloride.[2] Salt wastes from the manufacturing process have been deposited in two waste disposal ponds of approximately 120 acres (49 ha.) adjacent to the river. Mercury contamination in the North
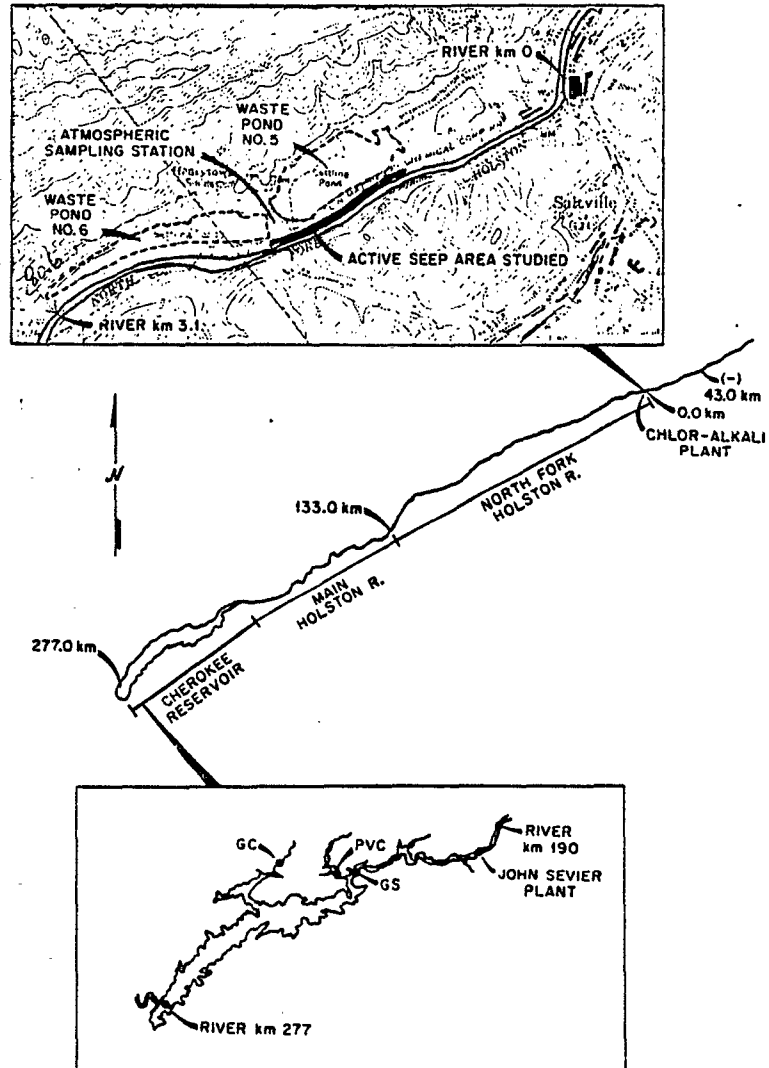
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Figure 4.1 Schematic of Holston-Cherokee System with detailed location of waste disposal ponds and sediment core stations in Cherokee Reservoir. GC = German Creek, PVC = Poor Valley Creek, GS = Galbraith Springs.

Fork was observed in 1970 and subsequent investigations have verified
the extent of contamination. [2-6]

The chlor-alkali plant was closed down in 1972 due to the high cost
of complying with existing water quality standards for chlorides, total
dissolved solids and mercury. [2] Our observations indicate that the plant
waste disposal ponds are a continuing source of mercury contamination in
the North Fork. [3]

The overall objective of our research on the Holston-Cherokee
system is to increase our understanding of the biogeochemical cycling
and transport of mercury in this contaminated environment. Specific
objectives include: 1) determine the distribution of mercury in water,
sediments, and biota of the Holston-Cherokee system to provide insight
into mechanisms of transport and bioaccumulation; 2) determine the
extent of continuing mercury input to the system; and 3) investigate
potential atmospheric emissions of mercury from existing waste disposal
ponds of the chlor-alkali plant.

In August 1974 and 1975 fish and benthic invertebrates were col-
lected at select stations on the Holston-Cherokee system. Fish were
collected by electrofishing and selective poison while benthic inverte-
brates were collected by disturbing river substrate upstream from a
collecting net. Fish and benthic invertebrates were processed and
analyzed for total and methylmercury by previously reported methods. [3,7,8]

Water samples were collected in 1975 by standard methods at select
stations. [9] Water samples to be analyzed for dissolved and particulate
mercury were filtered (0.45 µ) within five minutes of collection uti-
lizing a filtration system developed at our laboratory. [10] Routine

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handling of total water samples followed procedures previously described.[3]

Sediment samples in the North Fork Holston River were collected by hand in backwaters or by Ekman dredge depending on water depth. Core samples in Cherokee Reservoir were collected with a modified Livingston corer and samples from the waste disposal ponds were manually taken in polycarbonate or aluminum tubes. Sediment samples were wet sieved (44 µ or 2 mm standard sieve) and processed as previously reported.[3] The appearance and texture of the samples that were sieved through the 2 mm mesh indicated that they consisted of fine silts and clays (< 44 µ) and for our purposes can be considered as such. Water and sediment samples were analyzed for total mercury[7] and supportive chemical data were obtained following the methods in reference 11.

4.2.2 Geochemical Studies of Mercury. Table 4.1 summarizes relevant geochemical data collected during 1975. Stations are identified by river kilometer with the reference point located at the abandoned chlor-alkali plant (see Fig. 4.1 and Table 4.2). Replicate stations are described by identical locations but different sampling dates. The most striking patterns in the distribution of Hg in the system relate to the variations in bottom sediment Hg and total Hg in the water column with river kilometer (Fig. 4.2). The impact of mercury inputs from the waste disposal pond area on the Hg distribution in the NFHR is obvious considering the strong gradient of decreasing Hg concentration with distance downstream. An indication of temporal variability is shown as the range in total Hg concentration in the water for

Table 4.1. Distribution of mercury and other physical-chemical parameters for the Holston-Cherokee System at select stations in 1975.

Stations are river kilometers above (−) and below plant.

Station river km	pH	Specific conductance (μmhos/cm)	Chlorides (mg/l)	Dissolved organic carbon (mg/l)	Particulate organic carbon (mg/l)	Suspended solids (mg/l)	Total Hg water (μg/l)	Dissolved Hg water (μg/l)	Hg on suspended particulate (μg/g dry wt.)	Hg bed sediment (μg/g dry wt.)	Date
−43.0	8.0	248	1.8	2.16	−	12.6	0.070	0.001	5.80	.136	8 26
−14.0	8.3	253	4.2	1.62	−	11.2	0.025	ND^b	2.30	.118	8 26
−9.0	8.1	251	4.2	2.32	−	7.8	0.034	−	−	.165	8 26
−2.7	8.1	258	5.2	1.94	−	5.2	0.015	−	−	.114	8 27
−2.7	8.4	−^{a}	2.8	−	−	16.8	0.003	ND	−	−	5 21
−2.7	8.0	246	2.7	3.15	0.58	12.0	0.006	ND	0.36	−	7 29
−2.7	8.2	244	2.5	2.05	0.32	12.4	0.007	ND	0.55	−	7 30
−2.7	8.1	266	2.5	3.31	0.56	11.2	0.008	ND	0.65	−	7 31
3.1	8.2	5150	1490.0	2.71	−	8.9	0.210	0.056	13.70	11.50	8 26
3.1	8.7	448	156.0	−	−	9.8	0.093	0.047	5.30	−	5 21
3.1	8.1	1405	427.0	2.01	0.36	12.8	0.196	0.071	12.90	−	7 29
6.4	8.3	4000	1225.0	2.98	0.92	12.4	0.167	0.075	7.20	−	7 29
6.4	8.0	1280	358.0	3.60	0.30	14.8	0.185	0.050	10.90	−	7 30
6.4	8.1	5700	1848.0	3.05	1.22	4.2	0.193	0.074	5.00	−	7 31
9.7	8.2	1179	300.0	2.36	−	3.0	0.074	0.040	8.10	.20	8 26
17.0	8.2	1173	300.0	2.12	−	6.2	0.058	0.028	6.40	.30	8 26
21.0	8.4	1250	334.0	3.83	−	4.0	0.067	0.027	1.20	.40	8 26
43.0	8.1	821	216.0	2.60	−	12.2	0.032	0.021	0.57	.92	8 27
133.0	8.1	669	158.0	2.73	−	4.8	0.025	0.018		−	9 9
184.0	7.6	354	43.2	3.28	1.59	19.8	0.010	0.010	0.96	.52	9 9
190.0	7.7	205	12.6	1.94	1.02	3.8	0.029	0.005	0.26	−	9 9
277.0	8.5	224	14.1	1.81	0.70	3.8	0.006	0.004	1.20	−	9 10
277.0	7.7	245	14.0	1.72	0.74	21.0	0.009	0.006	0.29	.48	9 10
277.0	7.4	167	15.0	1.86	0.93		0.012				9 10
278.0	7.5	246	14.3	1.94	0.91	6.4	0.005	−	−	−	9 10

^{a} Not measured.
^{b} Not detected.

Table 4.2. Location of sampling stations on the Holston–Cherokee System

| Station description	Actual river mile	Miles above ( ) and below plant	Km above ( ) and below plant
North Fork Holston River			
Chatham Hill	109	26.5	43.0
Old Broadford	91	8.5	14.0
Neil Bridge	88.1	5.6	9.0
McCrady	85.9	3.4	5.5
USGS Station (0.4 mi below)	84.2	1.7	2.7
Chlor-Alkali Plant	82.5	0	0
Transect	80.6	1.9	3.1
Below disposal ponds	81.0	2.3	3.7
Railroad trestle	78.5	4.0	6.4
McKenna Island	76.5	6.0	9.7
Swinging bridge	72.0	10.5	17.0
Hayters Gap	69.5	13.0	21.0
Holston	59.5	23.0	37.0
Hines Island	56.0	26.5	43.0
Mendota	39	43.5	70.0
Hilton	22	60.5	97.0
Kingsport	0	82.5	133.0
Amis	110	114.5	184.0
Cherokee Reservoir			
H.B. Day Bridge	103	121.5	196.0
Malinda	98	126.5	204.0
Fall Creek Dock	81	143.0	230.0
25E Bridge	76	148.0	238.0
Cherokee Dam	52	172.0	277.0

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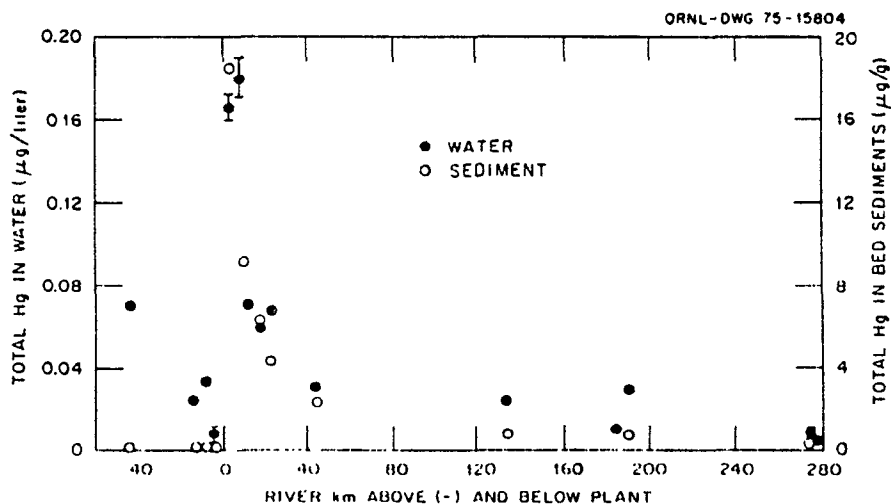
Figure 4.2   Distribution of total mercury in Holston River water (unfiltered) and sediment (dry weight) above and below the chlor-alkali plant in 1975.   Error bars = 1 S. D.

three stations near the source area (i.e., stations at -2.7, 3.1, and 6.4 km).

We have hypothesized that the main downstream transport of mercury from the source area in Virginia to Cherokee Reservoir occurs in the particulate phase.[3] If this is indeed the case, one would expect to find elevated concentrations of Hg in fine sediments (< 44 µ) which are deposited where the flow of the Holston is slowed upon entering quiescent waters (e.g., John Sevier Detention Lake and Lake Cherokee). Other factors, such as the source rocks of the sediments, being equal, fine-grained sediment inputs from other, presumably uncontaminated, tributaries such as Poor Valley Creek and German Creek should not show elevated mercury concentrations.

Table 4.3 describes the distribution of total mercury in size fractionated bottom sediments. The three areas involved include one station near the main river channel in the reservoir (Galbraith Springs) and two stations in delta areas of tributaries to the reservoir other than the Holston River itself (Poor Valley Creek and German Creek). These areas are illustrated in Fig. 4.1.

Table 4.3. Mercury concentrations in size fractionated
sediments from three tributaries of the Cherokee Reservoir.

Location	Depth (cm)	% <44 µ	Σ % OM	<44 µ % OM	Hg (ppm)		
					Σ	< 44 µ	>44 µ
German Creek[a]	0 5	40	2.7	7.4	0.146	0.290	0.050
	5 10	60	2.8	3.8	0.132	0.171	0.067
Galbraith Springs[b]	0 5	12	1.6	7.3	0 177	1.090	0.043
	5 10	12	1.1	7.4	0.152	0.890	0.052
Poor Valley Creek[c]	0 5	11	2.5	3.1	0.077	0.220	0.053
	5 10	50	3.5	5.1	0.111	0.135	0.061

[a]Station GC in figure 1
[b]Station GS in figure 1, located in the Holston R tributary
[c]Station PVC in figure 1

from Table 4.3

Depth cm	Σobs ppb Hg (whole sed)	<44 µ			>44 µ			Σ products ppb Hg	% recov
		wt fract	× ppb Hg	= Product	wt fract	× ppb Hg	= Product		
G. Creek 0-5	146	.40	290	116.	.60	50	30	146	1
5-10	132	.60	171	102.6	.40	67	26.8	129.4	9
Grab Spr 0-5	177	.12	1090	130.8	.88	43	37.8	168.6	9
5-10	152	.12	890	106.8	.88	52	45.8	152.6	10
P.V. Creek 0-5	77	.11	220	24.2	.89	53	47.2	71.4	9.
5-10	111	.50	135	67.5	.50	61	30.5	98.0	.88

% recovery calc'd as $\dfrac{\Sigma\ Products}{\Sigma\ obs} \times 100$

Results look very good.

Although the Hg concentrations in the unfractionated sediment samples are quite similar and do not indicate any disproportionate effect of the Holston River on the Hg burden of the reservoir, the concentrations in the < 44 μ fraction in sediments derived from the Holston River are elevated by a factor of 3-8 over the values for sediments derived from the other tributaries. Thus if the concentrations of mercury in similar size fractions, especially the easily transported sizes (< 44 μ) are compared, it is apparent that significant differences exist. The similarity in Hg concentrations in the < 44 μ sediment fraction at the Holston tributary station (Galbraith Springs) with the suspended sediments and fine bottom sediments collected at the river station 25 km upstream (station at river km 190, Table 4.2) lends considerable support to the above hypothesis. However, to completely study the question of Hg accumulation in the Cherokee reservoir system will require information on the historical variations in Hg concentrations of the < 44 μ sediment fraction in various locations in the lake where such sediments are and have been actively accumulating. The results of that study are pending and will be reported at a later date.

4.2.3 Mercury Distribution and Behavior in Fish and Benthos. The distribution of total mercury and percentage methylmercury in fish species and benthic invertebrate taxa collected in August 1974 at select stations is given in Tables 4.4-4.6. Mean total mercury levels well above the 0.5 ppm FDA guideline are evident in axial muscle of rockbass, hogsucker and shiners 3.1 and 21.0 km below the chlor-alkali plant, while mercury levels in rockbass 133.0 km below the plant are still in

Table 4.4. Total mercury (Σ Hg) and percentage methylmercury (% MeHg) in axial muscle of fish species at select stations on the North Fork of the Holston River, August 1974.

Σ Hg = μg/g wet weight ± 2 S.E., % meHg ± 2 S.E.

River kilometers above (–) and below plant

Species	-5.4 km		3.1 km		21.0 km		133.0 km	
	Σ HG	% MeHG	Σ HG	% MeHG	Σ HG	% MeHG	Σ HG	% MeHG
Rockbass (Ambloplites rupestris)	0.70 ± 0.23. n = 13 Size 7.8 – 303.2 g	88.7 ± 8.3 n = 10 Size 7.8 – 303.2 g	1.59 ± 0.33 n = 11 Size 19.6 – 184.3 g	83.7 ± 7.0 n = 7 Size 19.6 – 18 .3 g	1.14 ± 0.19 n = 16 Size 3.8 – 96.4 g	99.5 ± 4.0 n = 6 Size 3.8 – 96.4 g	1.26 ± 0.51 n = 10 Size 23.6 – 156.9 g	78.9 ± 16.9 n = 3 Size 23.6 – 156.9 g
Hogsucker (Hypentelium nigricans)	0.46 ± 0.19 n = 11 Size 11.8 – 191.0 g	103.8 ± 3.3 n = 9 Size 11.8 – 191.0 g	1.42 ± 0.16 n = 3 Size 41.2 – 113.2 g	90.9 ± 13.8 n = 3 Size 41.2 – 113.2 g	1.23 ± 0.13 n = 6 Size 43.0 – 164.1 g	86.3 ± 5.8 n = 6 Size 45.0 – 164.1 g	0.43 ± 0.11 n = 2 Size 53.4 – 55.6 g	84.6 ± 28.7 n = 2 Size 53.4 – 55.6 g
Shiner (Notropis spp.)	0.28 ± 0.05 n = 20 Size 7.0 – 47.1 g	84.5 ± 11.2 n = 10 Size 7.0 – 47.1 g	1.70 ± 0.51 n = 8 Size 1.6 – 3.7 g	105.1 ± 5.2 n = 3 Size 1.6 – 3.7 g	1.05 ± 0.17 n = 14 Size 1.3 – 22.2 g	83.8 ± 10.7 n = 5 Size 3.6 – 22.2 g	0.77 ± 0.15 n = 15 Size 1.2 – 7.9 g	79.2 ± 7.3 n = 6 Size 1.6 – 4.0 g

Table 4.5. Total mercury concentration (Σ Hg) and percentage methyl mercury (% MeHg) in benthic invertebrates collected at select stations, North Fork Holston River August 1974.

Total mercury values are ng/g wet weight (– – means taxa not present in enough quantity to analyze).

River kilometers above (–) and below plant

Taxa	-5.5 km		3.1 km		21.0 km		133.0 km	
	Total Hg	% MeHg	Total Hg	% MeHg	Total Hg	% MeHg	Total Hg	% MeHg
Hydropsychidae	– –	– –	1680	29.17	560	41.07	– –	– –
Corydalus	88	65.91	1940	40.72	640	49.20	222	62.93
Decapoda	65	51.81	– –	– –	1120	48.21	270	49.11
Psephenidae	16	37.5	– –	– –	– –	– –	– –	– –
Composite Benthos	35	51.43	1030	83.50	840	40.48	110	– –
Mean of taxa present[a]	51 ± 32	51.66 ± 11.60	1550 ± 541	51.13 ± 33.09	790 ± 250	44.74 ± 4.60	201 ± 95	56.52 ± 14.82

[a] Mean ± 2 S.E.

Table 4.6. Total mercury (Σ Hg) and percentage methylmercury (% MeHg) in axial muscle of fish species in Cherokee Reservoir, August 1974.

Σ Hg = μg/g wet weight ± 2 S.E., % meHg ± 2 S.E.

Species	River kilometers below plant					
	190.0 km		238.0 km		277.0 km	
	Σ HG	% MeHG	Σ HG	% MeHG	Σ HG	% MeHG
Largemouth bass (*Micropterus salmoides*)	0.34 ± 0.16 n = 12 Size 129.6 - 2072.7 g	92.5 ± 6.2 n = 10 Size 129.6 - 2072.7 g	0.11 ± 0.04 n = 20 Size 19.3 - 780.0 g	80.5 ± 9.5 n = 11 Size 19.3 - 780.0 g	0.19 ± 0.04 n = 16 Size 57.7 - 450.6 g	68.5 ± 5.7 n = 10 Size 57.7 - 450.6 g
Bluegill (*Lepomis macrochirus*)	0.32 ± 0.07 n = 20 Size 35.0 - 156.3 g	82.9 ± 13.5 n = 11 Size 35.0 - 156.3 g	0.13 ± 0.03 n = 20 Size 11.4 - 74.5 g	73.6 ± 11.7 n = 10 Size 11.4 - 74.5 g	0.15 ± 0.04 n = 20 Size 6.9 - 103.3 g	70.3 ± 12.2 n = 10 Size 6.9 - 103.3 g
Gizzard shad (*Dorosoma cepedianum*)	0.09 ± 0.02 n = 20 Size 2.1 - 284.0	77.3 ± 10.9 n = 11 Size 4.1 - 284.0 g	0.06 ± 0.01 n = 20 Size 2.4 - 133.8 g	61.7 ± 14.6 n = 10 Size 2.4 - 133.8 g	0.06 ± 0.005 n = 20 Size 18.0 - 174.0 g	70.1 ± 5.3 n = 10 Size 18.0 - 174.0 g
Threadfin shad (*Dorosoma petenense*)	0.05 ± 0.005 n = 20 Size 1.1 - 4.4 g	57.9 ± 6.8 n = 10 Size 1.3 - 4.4 g	0.03 ± 0.01 n = 20 Size 0.5 - 15.0 g	54.3 ± 13.6 n = 9 Size 0.9 - 2.0 g	0.05 ± 0.01 n = 20 Size 1.2 - 48.7 g	83.5 ± 5.9 n = 7 Size 10.3 - 48.7 g

excess of 1.0 ppm. The concentration of total mercury in rockbass and hogsucker 5.5 km above the plant approach or exceed 0.5 ppm which was unexpected for this control area. It is possible that localized movement of these species to and from the contaminated area below the plant could explain these slightly elevated levels. Fish species collected in Cherokee Reservoir on the whole contain muscle mercury below 0.5 ppm (Table 4.5).

Our observation that the majority of total mercury in fish muscle in the Holston-Cherokee system is methylmercury is in agreement with other investigators[12-19] (Tables 4.4 and 4.5).

Estimates of total mercury and percentage methylmercury in benthic invertebrate taxa collected in August 1974 on the North Fork are given in Table 4.6. Benthic invertebrates 3.1 km below the plant contain total mercury at about the same level (mean 1.550 ± 0.271 µg/g) as fish species (Table 4.4). Total mercury in benthic invertebrates 5.5 km above and 21.0 and 133.0 km below the plant appears to be lower than fish species at these stations (Tables 4.4 and 4.6). Mean percentage methylmercury in benthic invertebrates at all stations was on the order of 50% (Table 4.6) but considerable variability exists between taxa at any given station. The finding that on the order of 50% of total mercury in benthic invertebrates is methylmercury suggests that fish species in this system may derive a significant proportion of their methylmercury burden through feeding on benthic invertebrates.

Rockbass are predators feeding primarily on benthic invertebrates and smaller fish. Hogsuckers are bottom feeders and undoubtedly ingest benthic invertebrates as well as sediment. Shiners are predominately

insectivorous feeding on benthic invertebrates. The potential food web

consisting of rockbass-shiner-benthic invertebrate in the North Fork

enables a qualitative examination of food chain concentration of total

mercury. At the 3.1 km below the plant all links in this chain have

approximately the same mercury levels (Tables 4.4 and 4.5) indicating

mercury is not being magnified at the station most contaminated with

mercury. Mercury contamination due to sediments in the G. I. tract

of invertebrates may, however, mask this phenomenon. At the stations

5.5 km above and 133.0 km below the plant it appears that mercury con-

centration may increase with trophic level for these three taxa (Tables

4.4 and 4.5). It is possible that under high mercury contamination,

available mercury in water and sediments causes trophic accumulation

of mercury to be masked by direct accumulation from water.

Although incomplete, analyses of total mercury levels in fish

species collected in August 1975 (Table 4.7) indicate levels downstream

from the plant remain elevated. In 1975 we sampled farther upstream

(9.0 km) above the plant and it appears mercury levels are lower than at

5.5 km in 1974 (Tables 4.4 and 4.7).

The concentration of total mercury in fish species and benthic

invertebrates collected in August 1974 appears to follow the concen-

tration of total mercury in the water column and bed sediments at the

four stations sampled (Fig. 4.3). When the remaining samples of our

1975 collection are analyzed we will, through multivariate analysis

determine which factors in the abiotic environment account for the

variability in total mercury levels in fish species in this system.

Table 4.7. Total mercury concentration (Σ Hg) in axial muscle of fish species collected at select stations in the North Fork Holston River and Cherokee Reservoir in August 1975.

Σ Hg = μg/g ± 2 S.E.

| Species	North Fork Holston kilometers above (−) and below plant					Cherokee 277.0 km Σ HG
	−9.0 km Σ HG	3.1 km Σ HG	21.0 km Σ HG	43.0 km Σ HG	133.0 km Σ HG	
Rock bass (Ambloplites rupestris)	0.32 ± 0.09 n = 10 Size 9.3 – 133.9 g	- -	- -	1.29 ± 0.19 n = 10 Size 6.1 – 165.4 g	1.12 ± 0.57 n = 10 Size 42.0 – 112.7 g	- -
Hogsucker (Hypentelium nigricans)	0.28 ± 0.13 n = 10 15.3 – 274.2 g	2.14 ± 0.59 n = 10 36.3 – 311.4	1.66 ± 0.21 n = 10 37.4 – 250.3 g	1.11 ± 0.17 n = 10 18.2 – 471.1 g	0.82 ± 0.36 n = 10 48.6 – 385.4 g	- -
Shiner (Notropis spp.)	0.12 ± 0.03 n = 5 Size 7.8 – 12.0 g	2.12 ± 0.72 n = 5 Size 1.7 – 2.7 g	1.34 ± 0.51 n = 5 Size 9.2 – 11.2 g	1.43 ± 0.53 n = 4 Size 8.3 – 13.2 g	0.52 ± 0.51 n = 5 Size 8.4 – 12.3 g	- -
Largemouth bass (Micropterus salmoides)	- -	- -	- -	- -	- -	0.11 ± 0.09 n = 10 Size 23.9 – 1020.5 g
Bluegill (Lepomis macrochirus)	-	-	-	-	-	0.10 ± 0.02 n = 10 Size 11.6 – 139.0 g
Gizzard shad (Dorosoma cepedianum)	-	-	-	-	-	0.05 ± 0.007 n = 10 Size 133.7 – 250.79

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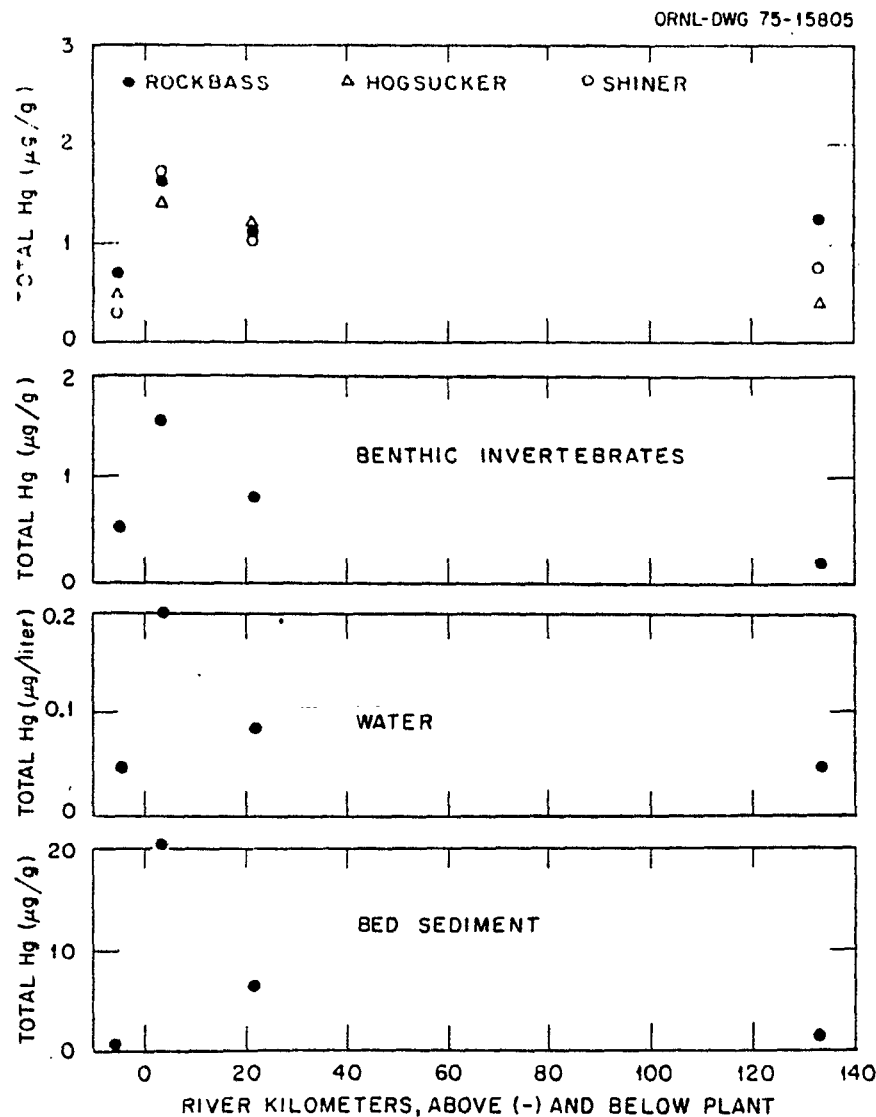
Figure 4.3   Distribution of total mercury in fish axial muscle (wet weight), benthic invertebrates (wet weight – whole animal), water (unfiltered) and bed sediment (< 44 μ dry weight) above and below the chlor-alkali plant on the Holston River in 1974.   Water and sediment data are from Reference 2.

In addition on-going research on the accumulation of mercury by fish species from sediments and the effect of organic ligands on mercury accumulation will provide a better understanding of the mechanisms of mercury uptake by aquatic biota.   A report of work still in progress will be submitted at a later date.

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4.2.4 Mass Balance for Mercury Near Saltville, Virginia. Accurate
quantification of the present rates of aqueous mercury input to the NFHR
from the waste pond system near Saltville is essential to the consideration
of continued contamination of the endemic biota and evaluation of any
future abatement measures. Leaching rates of mercury from the abandoned
plant waste disposal ponds were estimated during two hydrologically
contrasting periods (May 1975, river discharge at river km 3.1 12 m^3/sec
and pond surfaces partially inundated with water; and July 1975, river
discharge 1.8 m^3/sec, pond surfaces dry, seepage outfalls exposed).
Using the mass balance approach, leaching rates of mercury from the
waste disposal ponds were calculated as the difference between upstream
and downstream instantaneous mercury fluxes (in mass/time units)
assuming steady state conditions (Table 4.8). Based on mass balance
calculations from both sampling periods the flux of mercury in the NFHR
increases by a factor of approximately 30 between upstream (at river
km -2.7) and downstream (at river km 6.4) sites. It is also evident
that the net flux of mercury from the waste pond area does not exhibit a
linear relationship with river discharge. For example, although dis-

Table 4.8. Summary of mass balance determinations of mercury leaching rate
from the chlor-alkali plant waste disposal pond area, North Fork of the Holston River.

Date	Upstream[a]			Downstream[b]				Net flux (g/day)
	Total Hg (µg/l)	Stream discharge[c] (m^3/sec)	Total Hg flux (g/day)	Total Hg (µg/l)	% dissolved	Stream discharge[c] (m^3/sec)	Total Hg flux (g/day)	
5-21-75	0.003	11.5	2.98	0.094	52	12.2	99.1	96.1
7-29-75	0.006	1.70	0.88	0.167	45	1.92	27.7	26.8
7-30-75	0.007	1.61	0.98	0.185	27	1.81	28.9	27.9
7-31-75	0.008	1.57	1.09	0.193	38	1.77	29.5	28.4
7-31-75								14.2[d]

[a] 2.7 km above old chlor-alkali plant.
[b] 6.4 km below old chlor-alkali plant.
[c] Obtained by factoring discharge at USGS Sta. 03488000 located near Saltville by drainage area increase.
[d] Based on summation of measured fluxes of seepages from waste pond #5 and the major outfall from pond #6

charge was lower by a factor of 6.8 between the May and July measurement periods the net flux of mercury was lower by only a factor of 3.6. This may indicate that other factors such as antecedent hydrologic conditions of the waste ponds influence the Hg flux from this area.

Direct measurement of the mercury flux (14.2 g/day) from exposed seeps of the waste ponds on July 31, 1975 offers reasonable verification of the net fluxes calculated by upstream-downstream mass balance for the same period (28.4 g/day). Although this measured flux is only about half the calculated flux the agreement is not unreasonable given that only the most obvious and accessible seepages were measured. In any case these measurements and calculations point to the continued significance of the waste pond area as a source of Hg.

4.2.5 Laboratory Studies On Waste Pond Material. Very little is known about the horizontal and vertical distribution of mercury in the waste ponds or about the solubility of mercury in the waste material. It has previously been reported[3] that total mercury concentration in waste solids from the ponds is as high as 150 µg/g. More recent measurements at depths from 0-1.8 m in the waste ponds have revealed concentrations up to 350 µg/g. In order to determine what fraction of the total mercury in the waste is readily leachable by rainwater or actually dissolved in the interstitial water, waste material from the top and bottom of short cores collected in each pond was leached for 96 hours with rainwater. Table 4.9 summarizes the relevant results of this experiment as well as the experimental conditions. The most important implication of this simple experiment is that only a very small percentage (< 2% for Pond #5 and < 0.1% for Pond #6) of the waste-

Table 4.9. Summary of laboratory mercury leaching experiment using material from the
chlor-alkali plant waste disposal ponds

Values are means of duplicate experiments.

Sample location and depth	Total Hg in waste ($\mu g/g$)	Leachate pH	Leachate specific conductance ($\mu mhos/cm$)	Leachate Cl^- (mg/l)	Leachate dissolved Hg ($\mu g/l$)	% waste soluble[a]	% total Hg soluble[b]
Pond #5 0-2 cm	230	8.6	240	45	6.4 ± 1.2	1.2	0.14
Pond #5 36-38 cm	160	10.2	841	122	54.5 ± 6.5	4.4	1.78
Pond #6 0-8 cm	124	9.8	268	55	1.2 ± 0.2	1.6	0.05
Pond #6 8-27 cm	37	9.2	985	170	5.0 ± 0.7	5.8	0.07

[a]Two grams of waste material were shaken for 96 hours at ca. 25°C with 100 mls. of rainwater having pH = 3.8, conductance = 41 $\mu mhos/cm$, chloride = 0.03 mg/l and total Hg = 0.13 $\mu g/l$.

[b]Uncorrected for material dissolved in natural moisture of samples.

associated mercury was solubilized under the experimental conditions. This soluble fraction likely consists of aqueous mercury deposited when the pore water was removed during drying of the waste as well as readily soluble mercury associated with the solid material. It is also significant that concentrations of mercury observed in the leachate (30 $\pm$ 28 $\mu g/l$) were similar to observed concentrations in seepages from Pond #5 (40 $\neq$ 24 $\mu g/l$).

Although the total quantity of mercury remaining in the waste pond system cannot be accurately determined from our data, we can make an estimate based on core data from Pond #5. Mercury concentrations in these cores were found to be highest in the upper portion (350 to 4.4 $\mu g/g$ from 0-200 cm depth) but averaged 92 $\mu g/g$ (σ = 91, N = 17). An estimate of the total mercury burden of the upper two meters of Pond #5 can thus be calculated. Using the pond surface area of 2.9 x 10^5 m^2 and assuming a waste density of 2.0 g/cm^3 leads to a waste mass of $\sim 10^9$ kg. If the mercury content of this mass indeed averages 92 $\mu g/g$

then the total mercury burden of the upper two meters of Pond #5 is $\sim 9 \times 10^4$ kg. Assuming that less than 1% of this mercury is dissolved or readily soluble and using the leaching rate of mercury measured on July 31, 1975 for Pond #5 (14 g/day) we conclude that it would take on the order of 10^2 years to totally deplete Pond #5 of its soluble mercury burden. Since only the upper two meters of this pond were considered as a source for mercury in this calculation the estimate of flushing time is obviously minimal. Even so, the calculation points to the potential persistence of the mercury problem on the NFHR in the absence of abatement measures.

4.2.6 Atmospheric Emission of Mercury From Waste Ponds.

Elemental mercury ($Hg°$) is known to be a substantial fraction of the atmospheric mercury burden, especially near geothermal areas and mercury ore deposits.[20,21] Because of the high volatility of $Hg°$ as well as various organomercurials it is widely dispersed in the earth's atmosphere. Recently several papers have appeared concerning atmospheric Hg distributions in natural source areas,[20,21] ambient air in major cities distant from such areas,[22] and various sites known to be impacted by coal-fired power generation plants.[23-25] However, no information on such distributions or actual emissions from chlor-alkali plants or associated waste ponds exists, although studies concerning levels of $Hg°$ within certain workroom areas of the plants have been reported.[26,27]

We established an aerosol sampling station between the two waste ponds (Fig. 4.1) which would receive the greatest possible exposure to any emitted vapors. We collected duplicate samples of mercury vapor in filtered air (glass columns containing activated charcoal),[28] bulk

deposition (glass bottles), and total aerosol (0.4 µ nuclepore filter

collectors) from 1200 hrs. on 7/29/75 to 0700 hrs. on 8/1/75. The

results of the experiment are given in Table 4.10. For the period

sampled, wind direction recordings indicated the prevailing wind pattern

to be directly across waste pond #5 for 67% of the time (i.e., a NE wind),

across pond #6 for 17% of the time (SW wind), and from other directions

or calm for 16% of the time. The particulate Hg load was quite low

considering the area in question and may reflect the stability of the

waste pond surface to dust resuspension. The concentrations reported

here $(0.30 \pm 0.05$ ng/m^3) compare with values in the range of 1-9 ng/m^3

reported for ambient air in industrialized cities[29] and with values in

the range of 0.07-0.15 ng/m^3 in Walker Branch Watershed.[30] The actual

concentration of Hg on the aerosols in the wastepond area expressed as

ng of Hg per mg of particulate (ppm) is 5.7 ± 0.7 ppm compared to

4.0-8.8 ppm for Walker Branch Watershed aerosols. Thus there appears to

be no significant elevation in particulate Hg in the air near the waste

ponds during the period sampled.

Of most interest are the relatively high concentrations of gaseous

Hg measured. These values (991 ng/m^3) compare with concentrations in

the range of 0-49 ng/m^3 for air in the Tampa, Florida area[22] with $12 \pm$

Table 4.10. Estimates of atmospheric emission of mercury from the chlor-alkali plant waste disposal ponds.

Sample	Flow rate (l/min)	Volume sampled (m^3)	Total particulates (µg/m^3)	Hg load (ng/m^3)
Hg vapor #1	1.85	2.52		990
Hg vapor #2	1.77	2.41		992
Total aerosols #1	10.5	42.8	58.4	0.25
Total aerosols #2	9.3	38.1	63.0	0.36

7 ng/m^3 for air in Walker Branch Watershed, and with the EPA ambient air standard for total Hg of 1000 ng/m^3. Our finding that essentially 100% of the Hg in ambient air is present as a vapor agrees well with reported EPA tests (96% as vapor).[31]

It is possible to extrapolate the gaseous Hg results to determine an approximate emission rate for the waste pond area. However, an experiment has been designed to actually measure emissions from a known surface area of the waste ponds and will be reported at a later date. The important finding to date is that a previously unsuspected pathway for release of Hg from the waste pond area has been discovered, and that from July 29 to August 1, 1975 the air passing from waste Pond #5 to our adjacent sampling station approached the EPA ambient air limit for total mercury.

4.3 Walker Branch Watershed Studies

4.3.1 Introduction and Methods. There is mounting evidence[32-36] that many activities of man, particularly combustion of fossil fuels and industrial processing of metals and their ores, are responsible for elevated concentrations of many trace metals in the atmosphere and therefore potentially increased rates of transport to, and accumulation in, the landscape. Work of this project relates directly to quantification of atmospheric input, landscape cycling and hydrologic output of selected trace metals for the 97.5 hectare Walker Branch Watershed (WBW) which is impacted locally by emissions from three coal-fired steam plants. Specifically our research has the following objectives: 1) to derive relationships between levels of selected trace metals in air,

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